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Correlation between Magnetic Property and Cation Distribution in Z-type Hexagonal Barium-Ferrite ($\text{Ba}_3\text{Co}_{2-x}\text{Fe}_{24+x}\text{O}_{41}$) by Neutron Diffraction

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ABSTRACT

Z-type hexagonal ferrite samples in which cobalt is partially substituted with iron, $\text{Ba}_3\text{Co}_{2-x}\text{Fe}_{24+x}\text{O}_{41}$ ($x = 0, 0.2, 0.4, 0.6$), were prepared by the ceramic process under a sintering oxygen partial pressure, $P_{\text{O}_2} = 21.3$ or 101.3 kPa, at 1573 K. The influence of the substitution ratio and oxygen partial pressure on the complex permeability was investigated by examining the cobalt distribution over various cation sites in the Z-type structure with the neutron powder diffraction analysis performed at 294 K (neutron wave length was 1.006\AA). The neutron diffraction pattern was studied with the Rietveld method. A significant difference in the preferential occupation of cobalt on various kind of cation sites was observed between the samples obtained under $P_{\text{O}_2} = 21.3$ and 101.3 kPa. Almost all cobalt atoms are on the $12k$ octahedral site at the boundary between S- and R-blocks in the sample of $x = 0$, $P_{\text{O}_2} = 21.3$ kPa. On the other hand, in the sample of $x = 0$, $P_{\text{O}_2} = 101.3$ kPa, cobalt atoms are as well on other sites, the $12k$ octahedral site at the boundary between S- and T-blocks, the $4e$ tetrahedral site in S-block, the $2a$ octahedral site in T-block and the $2d$ five fold (trigonal bipyramid) site in T-block.

INTRODUCTION

In recent years, rapid progress of information society has been promoting downsizing of various electronic devices. In this trend, portable computer and mobile phone systems have been prevailing and becoming cordless, which needs improvements in the device integration technology and processing signals with much higher frequency (from MHz region to GHz). Electromagnetic noises radiated from these devices must be also in GHz region, so that obstruction and/or interference in normal operation are concerned [1]. Therefore, electromagnetic noise absorbent materials effective even in the GHz band have been required.

Z-type hexagonal barium ferrite $\text{Ba}_3\text{Co}_2\text{Fe}_{24}\text{O}_{41}$ is a promising candidate material because of its high permeability even at high-frequency region of GHz [2]. However, it is not easy to prepare the Z-type hexaferrite material as a single phase. Impurities of Y- ($\text{Ba}_2\text{Co}_2\text{Fe}_{12}\text{O}_{22}$) and W- ($\text{BaCo}_2\text{Fe}_{16}\text{O}_{27}$) phases easily occur and degrade resultant permeability because their intrinsic permeabilities are lower than that of the Z-type. We investigated synthesis conditions for obtaining single phase material of the Z-type hexaferrite varying temperature, oxygen partial pressure and substitution ratio of cobalt for iron. We found that a higher oxygen partial pressure and substitution of cobalt for iron are favorable for occurrence exclusively of the Z-phase and then for higher permeability [3]. We examined neutron diffraction (ND) patterns of the Z-phase samples by the Rietveld analysis in order to investigate sites occupied preferentially by iron or cobalt ions. We have already reported the results on iron-substituted

Z-type hexaferrite $\text{Ba}_3\text{Co}_{2-x}\text{Fe}_{24+x}\text{O}_{41}$ ($x = 0, 0.2, 0.4, 0.6$) sintered at $P_{\text{O}_2} = 101.3 \text{ kPa}$ [4]. In this paper, we report on results on the samples sintered at $P_{\text{O}_2} = 21.3 \text{ kPa}$ and compare them with the previous results in order to study correlation between the permeability and the site occupation preference.

EXPERIMENTAL

The samples with various compositions, $\text{Ba}_3\text{Co}_{2-x}\text{Fe}_{24+x}\text{O}_{41}$ ($x = 0, 0.2, 0.4, 0.6$) were prepared by the ceramic method as already reported [4]. Stoichiometric amounts of BaCO_3 , Co_3O_4 and Fe_2O_3 powders were mixed in a ball-mill with deionized water for 24 hours. They were dried and calcined at 1273K in air, crushed and shaped into pellets. They were then sintered at 1573 K for 16 hours under an oxygen partial pressure of 21.3 or 101.3 kPa. Their X-ray diffraction (XRD) patterns were measured in the range of diffraction angle $2\theta = 15 - 100^\circ$ at intervals of 0.02° . The neutron diffraction (ND) patterns at 294K were obtained by using the TAS spectrometer in a double axis mode at the beam line of KUR-TAS-B2 in Kyoto University Research Reactor. The sample powder was set in a vanadium cylindrical container with 20-mm diameter. The neutron flux at the sample position was about $10^5 \text{ cm}^{-2} \text{ s}^{-1}$. The diffraction angle 2θ was traced in the range of $7.5 - 42.5^\circ$. Its angle step $\Delta 2\theta$ was 0.1° and the measured time at each step was 90 s. These XRD and ND diffraction patterns at room temperature were examined with the Rietveld method analysis in order to optimize parameters regarding the crystal structures [5]. The XRD data was first analyzed for determining atomic coordinates and lattice parameters, and then the ND pattern was analyzed for determining the distribution of magnetic ions Fe and Co.

CRYSTAL STRUCTURE OF Z-TYPE HEXAGONAL FERRITE

The crystal structure of the Z-type hexagonal ferrite, $\text{Ba}_3\text{Co}_2\text{Fe}_{24}\text{O}_{41}$, is a complex one which consists of 44 atomic layers stacking up along the c -axis. In this structure, S, R and T blocks are ordered as $\text{RSTSR}^*\text{S}^*\text{T}^*\text{S}^*$, where the asterisk indicates rotation of each block by 180° around the c -axis. Figure 1 describes a part of atomic arrangement on (110) plane, in which iron and

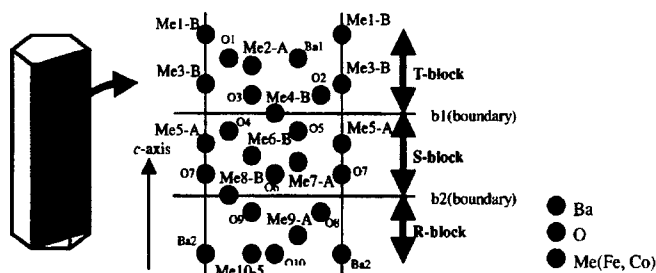


Figure 1. Partial schematic illustration of atomic sites in Z-type hexagonal ferrite as a view from $[110]$ direction. Attached labels are mentioned in the text.

cobalt, represented as Me, are not distinguished. Me4 and Me8 sites are respectively on boundaries of T-S and S-R and labeled b1 and b2. Attached marks to the labels, -A, -B and -5, show that each Me ion are in tetrahedral, octahedral, and five fold (trigonal bipyramid) sites, respectively. The crystal structure is represented by a space group of $P6_3/mmc$, and, ideal atomic coordinates and lattice parameters were reported as $a = 5.88 \text{ \AA}$, $c = 52.31 \text{ \AA}$ by Vinnik [6]. Atomic coordinates of Ba, Me (Co and Fe) and O given by this space group are tabulated in Table 1. Ba ions are distributed over two sites labeled Ba1 and Ba2, and iron and cobalt ions over ten sites labeled Me1-Me10 [7].

RESULTS AND DISCUSSION

First, we performed XRD pattern refinement starting with the ideal atomic coordinates tabulated in Table 1. In this refinement, we have imposed several restrictions on performing refinements; (1) only Z-coordinates are allowed to change, while X- and Y-coordinates are kept constant. (2) two sites on a plane normal to c-axis share a Z-coordinate; Ba1-O1, O2-O3, O4-O5, O6-O7 and O8-O9. (3) atomic coordinates of Ba2, Me1, Me10 and O10 are kept constant in order to conserve the crystal symmetry. Me1-Me10 sites for iron or cobalt ions are assumed to

Table 1. Initial Atomic coordinates of Z-type hexagonal ferrite and Results of the Rietveld for X-ray and Neutron Diffraction of $P_{O_2} = 21.3 \text{ kPa}$.

Space group $P6_3/mmc$			Initial atomic coordinates of $Ba_2Co_2Fe_{24-x}O_{41}$			Refined structural parameters for $Ba_2Co_2Fe_{24-x}O_{41}$											
Sites Description			$a = 5.88 \text{ (\AA)}$ $c = 52.31 \text{ (\AA)}$			$x = 0$ $a = 5.8774$ 52.259		$x = 0.2$ 5.8791 52.255		$x = 0.4$ 5.8796 52.242		$x = 0.6$ 5.8781 52.236					
Label	Wyckoff	Block	x	y	z	z		z		z		z					
Spin dir.	letter					XRD	ND	XRD	ND	XRD	ND	XRD	ND				
Me1-B ↑	2a	T	0	0	0	0	0	0	0	0	0	0	0				
Me2-A ↓	4f	T	1/3	2/3	.0341	.0331(9)	.0299(1)	.0348(9)	.0339(3)	.0363(9)	.0296(5)	.0360(4)	.0364(9)				
Me3-B ↓	4e	T	0	0	.0454	.0556(1)	.0605(3)	.0535(3)	.0579(9)	.0530(9)	.0543(9)	.0566(2)	.0566(9)				
Me4-B ↑	12k	b ₁	1/2	0	.0909	.0908(2)	.0900(5)	.0912(3)	.0941(5)	.0913(5)	.0902(5)	.0910(5)	.0933(9)				
Me5-A ↓	4e	S	0	0	.125	.1285(7)	.1291(5)	.1287(3)	.1252(1)	.1275(1)	.1199(4)	.1275(8)	.1240(5)				
Me6-B ↑	4f	S	1/3	2/3	.1364	.1384(6)	.1467(7)	.1376(2)	.1394(3)	.1373(0)	.1517(9)	.1384(8)	.1396(5)				
Me7-A ↓	4f	S	2/3	1/3	.1477	.1498(3)	.1533(9)	.1508(7)	.1488(2)	.1501(0)	.1479(0)	.1519(3)	.1505(9)				
Me8-B ↑	12k	b ₂	1/6	1/3	.1818	.1867(8)	.1903(3)	.1861(7)	.1879(4)	.1873(4)	.1942(1)	.1868(8)	.1883(3)				
Me9-B ↓	4f	R	2/3	1/3	.2273	.2201(8)	.2235(4)	.2236(9)	.2245(1)	.2212(1)	.2252(6)	.2236(1)	.2260(1)				
Me10-S ↑	2d	R	1/3	2/3	.25	.25	.25	.25	.25	.25	.25	.25	.25				
Ba2	2h	R	0	0	.25	.25	.25	.25	.25	.25	.25	.25	.25				
Ba1	4f	T	2/3	1/3		.0227	.0274(7)	.0268(9)	.0277(9)	.0279(9)	.0277(2)	.0356(3)	.0271(2)	.0265(9)			
O1	12k	T	1/6	1/3													
O2	12k	T	1/3	1/6		.0682	.0655(9)	.0435(0)	.0699(9)	.0685(3)	.0873(2)	.0926(1)	.06816(6)	.0688(0)			
O3	4f	T	1/3	2/3													
O4	12k	S	1/6	1/3		.1136	.1059(4)	.1023(4)	.1091(1)	.1108(7)	.1207(5)	.1215(1)	.1111(3)	.1120(8)			
O5	4f	S	2/3	1/3													
O6	12k	S	1/2	0		.1591	.1587(9)	.1586(4)	.1576(3)	.1640(8)	.1553(7)	.1587(3)	.1566(6)	.1641(3)			
O7	4e	S	0	0													
O8	12k	R	1/3	1/6		.2045	.1989(1)	.2030(2)	.1986(6)	.2122(3)	.1907(7)	.1866(2)	.1999(1)	.2110(2)			
O9	4f	R	1/3	2/3													
O10	6h	R	0	1/2	.25	.25	.25	.25	.25	.25	.25	.25	.25				
S-parameter						3.93	3.61	2.62	2.97	4.17	3.58	3.42	2.8				

Remark) Coordinates in italic are invariables.

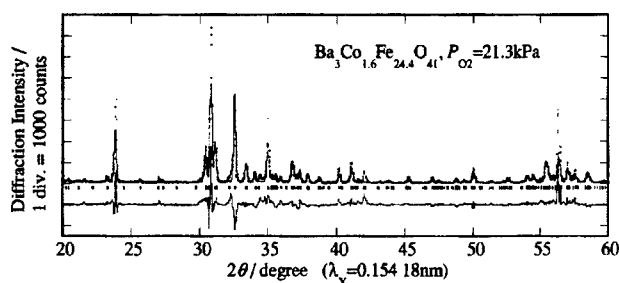


Figure 2. A typical result of present Rietveld refinement for XRD diffraction patterns of $P_{O_2} = 21.3$ kPa.

be filled only with iron, because X-ray scattering factors of iron and cobalt ions are almost same and they are indistinguishable. Thus optimized atomic coordinates and lattice parameters, shown in Table 1, were then submitted to ND pattern refinement. On the ND pattern refinement, another three restrictions were imposed in addition to those mentioned above; (4) the valences of iron and cobalt ions are Fe^{3+} and Co^{2+} , and the moment sizes are $5 \mu_B$ and $3 \mu_B$, respectively. (5) the valence of iron ion substituted for cobalt is Fe^{2+} with moment size of $4 \mu_B$. (6) these moments orientate up or down as shown in Table 1 [9]. Thus optimized atomic coordinates are as well tabulated in Table 1 for comparison with those obtained from XRD data.

Typical results of the present Rietveld analyses for XRD and ND are respectively shown in Figs. 2 and 3, in which experimental plots and refined patterns are together. Both are for the samples sintered at $P_{O_2} = 21.3$ kPa. It is noticed that deviation of the profile from the data around peaks due to (00 l) planes was of significance in the XRD refinements whilst not in the ND. This significant deviation is reasonably ascribed to preferential orientation of (00 l) planes normal to the XRD specimen plate [4, 8]. The sample of the ND was just a powder charged into a cylinder without any compression and therefore free from such orientation. The S-parameters associated with the present refinements are given at the bottom of the table.

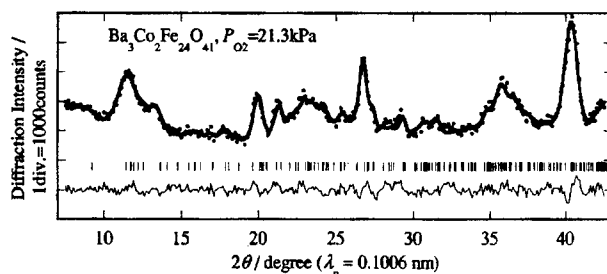


Figure 3. A typical result of present Rietveld refinement for ND diffraction patterns of $P_{O_2} = 21.3$ kPa.

Table 2. Iron and Cobalt site distribution determined by the Rietvelt refinements of the neutron diffraction data of $P_{O_2} = 21.3$ kPa.

Label, Spin direction	Site	Multiplicity Wyckoff letter	Block	g: Fractional Occupation Number							
				$x = 0$		$x = 0.2$		$x = 0.4$		$x = 0.6$	
				Fe	Co	Fe	Co	Fe	Co	Fe	Co
Me1-B ↑	2a	T	T	0.96	0.04	0.96	0.04	0.98	0.02	1	-
Me2-A ↓	4f	T	T	1	-	1	-	1	-	1	-
Me3-B ↓	4e	T	T	1	-	1	-	1	-	1	-
Me4-B ↑	12k	b1	T	1	-	1	-	1	-	1	-
Me5-A ↓	4e	S	S	0.98	0.02	0.99	0.01	0.98	0.02	1	-
Me6-B ↑	4f	S	S	1	-	1	-	1	-	1	-
Me7-A ↓	4f	S	S	1	-	1	-	1	-	1	-
Me8-B ↑	12k	b2	T	0.68	0.32	0.71	0.29	0.74	0.26	0.77	0.23
Me9-B ↓	4f	R	R	1	-	1	-	1	-	1	-
Me10-S ↑	2c	R	R	1	-	1	-	1	-	1	-
Magnetic moment angle ϕ with c-axis				83°		90°		90°		84°	

Previous our measurements on temperature dependence of the ND patterns clearly indicated that the peaks in a range of $10 - 15^\circ$ are caused by the magnetic scattering from ordered magnetic ions [4]. The Rietveld refinement of the ND patterns can, therefore, throw light on the distribution of iron and cobalt ions over the ten sites, Me1-Me10, and orientation of the magnetic moment. Table 2 shows thus estimated occupation ratios of cobalt located in these sites and angle between the moment vector and the c -axis. Magnetic moment angles with c -axis listed at the bottom were found to be almost 90° . Cobalt ions were found to be located only in four sites out of the ten, Me1-B↑, Me5-A↓, Me8-B↑, and Me10-S↑, as has been found with samples sintered under $P_{O_2} = 101.3$ kPa [4]. Figure 4 shows the occupation numbers of cobalt for the four sites, which are obtained by multiplying the occupation ratio by each site number. The present results for $P_{O_2} = 21.3$ kPa are shown on the right-hand side, while the previous our results for $P_{O_2} = 101.3$ kPa on the left-hand. A clear difference is noticed between the right- and the left-hand: Cobalt ions are distributed over the four sites in the left-hand side while substantially only on a site, Me8↑, in the right-hand. When x increases, substituting Fe^{2+} ions for cobalt go dominantly into Me1-B↑(2a) in case of 101.3 kPa, while into Me8-B↑(12k) in case of $P_{O_2} = 21.3$ kPa.

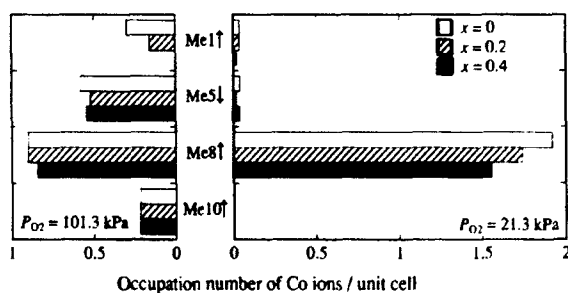


Figure 4. The occupation number of cobalt ions in $Ba_3Co_2Fe_{24-x}O_{41}$.

Now we examine correlation amongst thus estimated spin orientations of the sites, moment sizes of ions located there and resultant permeability. As shown in Table 1, there are 32 ions with up-spin and 20 with down-spin in the unit cell. The present our results indicates that, in the sample sintered under $P_{O_2} = 101.3$ kPa, the down-spin site, $Me5\downarrow$, is significantly occupied by cobalt with smaller magnetic moment, $3\mu_B$, than that of iron, which contributes to an increase in saturation magnetization and then permeability. However, any down spin site seemed not to be occupied by cobalt when $P_{O_2} = 21.3$ kPa. Recall here that the permeability of $P_{O_2} = 101.3$ kPa was larger than that of $P_{O_2} = 21.3$ kPa [3]. These facts are consistent with each other, which would support reliability of the present analyses and results regarding preferential site occupation by cobalt and iron ions.

CONCLUSION

We investigated correlation between permeability and magnetic cation distribution in $Ba_3Co_{2-x}Fe_{24+x}O_{41}$ ($x = 0, 0.2, 0.4, 0.6$) prepared by the ceramic method under oxygen partial pressure $P_{O_2} = 101.3$ and 21.3 kPa, and found; (1) Cobalt ions occupy almost a particular site (12k) out of 10 sites for $P_{O_2} = 21.3$ kPa, while 4 sites (12k, 4e, 2a and 2d) for $P_{O_2} = 101.3$ kPa. (2) The additional Fe^{2+} ions are mainly substituted for cobalt in 2a site for $P_{O_2} = 101.3$ kPa, while 12k site of $P_{O_2} = 21.3$ kPa.

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